DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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SUMMER INTERNSHIP AT DOE HEADQUARTERS OFFICE OF GROUNDWATER AND SOIL (EM-22)

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ABSTRACT

The Department of Energy (DOE) Environmental Management (EM) was established in 1989 to achieve safe and compliant disposition of defense nuclear legacy wastes. The unique contamination profiles of hundreds of plumes located at different sites around the country make the remediation process unprecedented in scope and complexity. As a result of this, groundwater and soil contamination, more than any other, provides the greatest uncertainty since it cannot be seen or touched and therefore relies heavily on strong science and engineering techniques.

This report includes a summary of the mercury remediation and characterization action area as it pertains to the Office of Groundwater and Soil as well as a project proposal review performed for the Strategic Environmental Research and Development Program (SERDP) and the Experimental Program to Stimulate Competitive Research (DOE EPSCoR). The reviews were done to determine whether or not the proposal is likely to achieve its stated goals under the proposed conditions and to ascertain its eligibility for resource allocation.

The tasks performed during the summer 2009 internship contributed to the vision and mission of the Office of Groundwater and Soil to build stronger collaborations with the science and engineering community and to become recognized as “Best-in-Class” and the “Technical Authority” in groundwater and soil remediation.

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1. INTRODUCTION

The Department of Energy (DOE) Environmental Management (EM) was established in 1989 to achieve safe and compliant disposition of defense nuclear legacy wastes and manage facilities at 60 sites in 22 states. At these sites, a total of 200 contaminated plumes have been identified. The unique contamination profiles of these plumes make the remediation process unprecedented in scope and complexity. This complexity lies in the fact that technologies for the successful disposition of wastes either have not yet been developed or require significant re-engineering to meet EM needs. Groundwater and soil contamination, more than any other, provides the greatest uncertainty since it cannot be seen or touched and, therefore, relies heavily on strong science and engineering techniques.

The Office of Groundwater and Soil focuses on six major action areas which are linked by an overall remedial strategy:

1. Advanced Remediation Methods for Metals and Radionuclides in the Vadose Zone
2. Attenuation-Based Remedies for Chlorinated Solvents in the Vadose Zone and Groundwater
3. Attenuation-Based Methods for Metals and Radionuclides in Groundwater
4. Mercury Characterization and Remediation
5. Advanced Subsurface Computing for Environmental Management (ASCEM)
6. Landfills and Disposal Area

In the summer of 2009, DOE Fellow, Rosa G. Ramirez, participated in a summer internship for the Office of Groundwater and Soil, assisting in managing and coordinating mercury-related research and remediation activities as well as reviewing project proposals. In addition, Ms. Ramirez was involved in revising the 2009 DOE Groundwater Plume Maps booklet and associated groundwater database. This booklet is annually compiled by the Office of Engineering & Technology and will show the characteristics of contaminant plumes as well as the status of contamination and remedial approaches at major DOE sites in order to aid in the decision making for remediation prioritization. This report will give an overview of the tasks Ms. Ramirez performed during the internship, focusing on the project proposals that were reviewed, as well as the mercury characterization and remediation action area in which she was extensively involved.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE/FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2009, a DOE Fellow (Rosa Ramirez) spent 10 weeks doing a summer internship at DOE Headquarters in the Office of Groundwater and Soil (EM-22) at Germantown, MD, under the supervision and guidance of Skip Chamberlain and Dr. Karen Skubal. The DOE Fellow's project was initiated on June 1, 2009, and continued through August 7, 2009, with the objective of assisting the coordination and management of mercury-related research and remediation activities for DOE's Oak Ridge Reservation in Tennessee. Concurrently, the intern reviewed project proposals, examining the past performance of the proposed technology and the conditions under which it was used, assessing its limitations and any problems that may have occurred. This information was used to determine whether or not the proposal is likely to achieve its stated goals under the proposed conditions and to ascertain its eligibility for resource allocation. In addition, the intern was involved in revising the 2009 DOE Groundwater Plume Maps booklet and associated groundwater database. This booklet is annually compiled by the Office of Engineering & Technology and will show the characteristics of contaminant plumes as well as the status of contamination and remedial approaches at major DOE sites in order to aid in the decision making for remediation prioritization.

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3. MERCURY REMEDIATION AND CHARACTERIZATION

Mercury was used in large quantities at the Y-12 National Security Complex during the 1950s and early 1960s as part of a lithium separation process. During this period, large quantities of mercury were released to the environment, resulting in the contamination of buildings, soils, sediments, groundwater and surface water. The behavior of mercury in the environment is complex, and remediation presents major challenges:

- The benefits and objectives for mercury remediation activities lack specificity and clarity.
- While mercury source reduction is a regulatory driver, no direct linkage exists between mercury source reduction and emerging stream protection endpoints such as mercury levels in fish tissue.
- The technical basis and defensibility of waste characterization and segregation and technology selection should be a primary focus of future Integrated Facilities Disposition Project (IFDP) planning.
- Estimates of mercury-contaminated materials will likely increase as buildings are decontaminated and decommissioned.
- The closing of the Nevada Test Site mixed waste disposal facility in 2010 may present a major programmatic risk factor and should be factored into decisions concerning the expansion of the on-site Environmental Management Waste Management Facility (EMWMF) and the possible construction of a new EMWMF.

3.1 Mercury Summit

Technical exchange concerning mercury issues and potential remediation approaches at Oak Ridge can help DOE to plan and prepare for remediation activities as the IFDP is implemented. A technical summit to facilitate the exchange of information and ideas concerning mercury-related issues will be held at Vanderbilt University in late 2009. Participants will include representatives from government, academia, industry, state and federal regulatory agencies, as well as other stakeholders. Development of the summit will be guided by a steering committee comprised of Skip Chamberlain (DOE EM), Jim Clarke (VU/CRESP), Rich Landis (DuPont), Brian Looney (Savannah River National Laboratory), and Dawn Kaback (AMEC/Geomatrix), with assistance from EM staff.

The summit will focus on information exchange; identification of best practices for mercury characterization, site assessment, and remediation; and development of research priorities with an emphasis on Oak Ridge site needs. Presentations will be given by experts and practitioners in areas including:

- Mercury-related regulatory issues at Oak Ridge
- Oak Ridge site needs and remediation technology evaluation and planning
- Modeling and characterization of potential mercury source areas and associated fluxes
- Mercury biogeochemistry and the characterization and behavior of mercury in environmental media

- New technologies for mercury removal or control, including soil and sediment amendments
- Assessment of toxicity and ecological risk for mercury-contaminated media
- Experience at other sites with remediation technologies and approaches for mercury-contaminated media

The product of the meeting will be a compendium organized by session topic. Each section will begin with a brief white paper that identifies data gaps, research needs and research priorities. It will summarize the major conclusions and recommendations derived from presentations and discussions held during the session. The white paper will be followed by presentation materials provided by the session speakers. The compendium will be prepared in the weeks following the summit and will be distributed to the participants. The ultimate goals of the mercury summit are: the prioritized identification of research needs and associated budget requirements; improved communication among research teams, site personnel and regulators; and, potentially, the development of a partnership that would include representatives from DOE, regulatory agencies, academia and industry to facilitate addressing the needs identified by the summit.

4. SERDP PROJECT PROPOSALS

The Strategic Environmental Research and Development Program (SERDP) has been established by the Department of Defense (DoD) to focus on the environmental problems that their projects may or may not cause in order to be able to reduce future and current environmental liabilities. SERDP works together with the Department of Energy and the Environmental Protection Agency. Following are two of the most representative SERDP projects reviewed:

4.1 The Importance of Sorption in Low-K Zones on Chlorinated Solvent Plume Longevity in Sedimentary Aquifers

Summary:
Evaluate the relative impacts of K and sorption heterogeneity on CVOC mass storage, mass removal and concentration reduction in sedimentary aquifers.

1. Rather than the current expectation of low and linear sorption in all systems, high non-linear sorption may be the most appropriate default expectation for persistent COV plumes.
2. The project will define the conditions in which to employ the new paradigm of high and nonlinear sorption.
3. Investigate the importance of coarse porous lithocomponets on mass storage and delayed release.
4. Simulations will employ detailed lithofacies maps and associated K and sorption properties measured by facies.
5. Improved methods for site assessment will be developed to build on a geological conceptual model.
6. The project will evaluate the fundamental processes that control mass storage and release from the grain to the aquifer scale allowing us to evaluate the governing processes at each scale and overall.

Review:
Task 1: Will determine retarded CVOC diffusion using high sorbing, low carbon content aquifer lithocomponents and aquitard material to evaluate the impact of nonlinear sorption at the (sub) grain scale.

- The hypothesis in this section is that release in low K zones is concentration dependant though diffusion. However, to evaluate the concentration effects on desorption rate, flow should be considered since this will cause more erosion and, therefore, more shearing stresses.
- Since the concentration gradient will be the driving force of this process, they should specify what kind of liquid will be used to test the aquitard and the two lithocomponent materials, as well as the components and concentration this solution will have. They only specify the different concentrations the actual aquitard will have. Will they use different concentrations of solution as well?

- For the desorption experiments, they are trying to produce a uniformly compact aquitard material at a specific constant initial concentration. However, these aquitards are rarely found with such ideal conditions, since they tend to decrease in porosity as their center is approached. This approach will fail to represent actual conditions.

Task 2: Will map lithofacies at two outcrop analog field sites to provide an authentic geologic framework in order to constrain the spatial distributions of both K and sorption heterogeneity.

- In this section, they mention that they do not have geochemical data from this site (Morrison Formation near San Ysidro). However, they state that the sandstone has greater physical heterogeneity compared to previously observed sites. Therefore, it would be more useful to do this geologic characterization (Task 2) before Task 1. In this way, they will not use estimates such as grain size distributions on the studies on Task 1, and they will not have to repeat those experiments once the geologic characterization is done. More accurate results would be obtained in this way.

Task 3: Consists of numerical experiments designed to "upscale" the results of laboratory studies (Task 1) to assess the role of intragranular diffusion and sorption processes on contaminant tailing.

- In this section, they will consider sorbent type, fraction of sorbent present and particle size as source conditions. However, they will use a 'constant' sorption parameter (isotherm and diffusion constant), which they will obtain from Task 1. This will only give skewed results. If they wanted to use results from Task 1, they should further develop the studies done there. Task 1 will be performed under too basic conditions since only 2 types of materials will be studied. The paper is called "The Importance of Sorption;" therefore, more than a constant sorption value should be used for the modeling.

Task 4: Will quantify the impacts of sorption and K spatial heterogeneity on tailing using high resolution, stratigraphically realistic system(s) as determined in Task 2.

- This task will also use results from Task 1 as sorption parameters.
- Considering only equilibrium sorption is considered here and the fact that this model only allows for large contrasts limiting variability within inclusions, Task 4 should be merged with Task 3.

Task 5: Will integrate findings from Tasks 1-4 along with selected large scale multi-process simulations. The findings will be used to populate a practical decision matrix to aid practitioners in site assessments and remedy planning.

4.2 Bioavailability and Methylation Potential of Mercury Sulfides in Sediment

Summary:

The authors of this proposal hypothesize that "kinetically-limited mercury sulfide mineralization reactions, rather than equilibrium porewater chemistry, control the concentration of bioavailable mercury to sediment bacteria that convert it to MeHg."

1. The research intends to determine how mercury sulfide becomes biologically available to anaerobic bacteria, which converts it to methyl mercury (MeHg).
2. The scientists suggest that "aging" of mercury sulfide (HgS) is responsible for increasing bioavailability of mercury to bacteria.
3. Aging causes bulk HgS to decay into nanoparticles of HgS.
4. HgS nanoparticles are hypothesized to be more bioavailable because the particles are more able to collect near methylating bacteria than the bulk material.
5. The results of the study will be incorporated to a model that describes mercury fate in porewater.

Review:

Research Methods: Section 3.2
Task 1: Assess methylation rate of HgS nanoparticles by sulfate-reducing bacteria and compare the rates to those for bulk metacinnabar.

- The authors of the proposal have no clear declaration of what the control for the experiment is. What standard do they intend to use to determine an increase in MeHg production by bacteria?
- What precautions will be in place to prevent the growth of HgS grains in the solution? Nanoparticles tend to agglomerate and form bulk material.

Task 2: Confirm the delivery and uptake of Hg to the cell.

Task 3: Evaluate mechanism of nanoparticle stability, incorporating chemical complexities associated with sediment porewater chemistry.

- An experiment will be performed to determine HgS stability under a particular set of soil parameters. What data will be collected to determine if the parameters determined from the experiments are consistent with true soil conditions? The need to determine the role of nanoparticle HgS is diminished if it is only stable in a very narrow range of parameters.

Task 4: Develop quantitative relationships between environmental parameters and MeHg production in sediment environments.

- This task relates to the construction of a quantitative model to determine the fate of mercury species. Validation of the model will be done with the results from Tasks 1-3, but will this model hold true for other environmental conditions? Are there plans to determine if this model is viable at other sites?

5. EPSCoR PROJECT PROPOSALS

DOE's Experimental Program to Stimulate Competitive Research (DOE EPSCoR) is a federal-state partnership program created with the goal of providing incentive energy related research and development across the nation. This program supports DOE's mission of establishing energy security to the United States while further developing both economically and scientifically. The mission of DOE EPSCoR is to support basic research activities spanning the broad range of science and technology programs within DOE and to increase the number of scientists and engineers in energy-related areas. Following are the most representative EPSCoR project reviews:

5.1 Review of IMPACT Services' GeoMelt Demonstration for TRU Waste Shafts Proposal

IMPACT service's GeoMelt division is proposing to demonstrate the treatment of transuranic (TRU) waste using their Subsurface Planar Vitrification (SPV) technology. The goal is to show that the use of this technology is more effective when compared to current conventional techniques. It also claims to enhance worker safety and cost effectiveness. The demonstration will involve Shafts 222 and 223 at LANL's MDA-G.

The proposers of this project are attempting to maximize results by anticipating the possible modes by which the experiment may fail and by providing advanced remediation. Some of these remediation modes involve physical barriers, such as a protective refractory wall, to limit the thermal effects and mobility of the vitrified materials, and fume hoods to capture escaping gases. An important consideration is that there is no mention of how a barrier may be constructed below the surface, and if excavation is required to put this barrier in place. This process may defeat the purpose of the subsurface vitrification as this will expose workers to radioactivity and toxic contaminants.

The current remediation process includes a significant number of safe guards to prevent the release of contaminants and to isolate the radioactive material from the work force. This method is safe but not cost effective, and two issues arise from it. The first issue is the possibility of human exposure during excavation. The second issue is cost due to sorting of untreated TRU waste. The claim made in this particular proposal is that by vitrifying the material in situ underground, the amount of exposure to radioactivity can be reduced through an inherent shielding effect that occurs in the glass. This is a true statement when considering that studies have shown a significant reduction in surface particle radiation of the glass. What receives little mention is whether or not there is as significant a decrease in gamma radiation levels. This lack of conclusive evidence can cause an underestimation of exposure levels.

In addition, past studies have shown that the radioactivity of the final product is reduced at the surface but increases towards the center. Therefore, little homogeneity of radiation is shown. This issue is very important when it comes to excavating the vitrified solid out of the soil. Even though the excavation and removal process is not detailed on the proposal, they do

show pictures in which the vitrified solid is being broken into pieces for removal. This is a hazard not only to the workers, since they will be exposed to higher levels of radiation as the drill goes deeper into the solid, but it also spreads contamination to the surrounding soil since smaller particles will not be easy to control. IMPACT services claim the ability to perform vitrification in situ will reduce costs significantly. Although the process may reduce the clean up costs, a permanent site to process this new material is necessary, therefore, adding to the necessary budget.

The proposed activities achieve the goals of the project in certain aspects of the process; however, new situations that arise need to be further investigated to determine their actual effects on safety and cost. Under certain conditions, this technology may achieve its goals, for instance, for low-level radioactive waste. Past evidence has shown that this process does reduce the radioactivity of the original material but not completely. Therefore, having a low-level radioactive waste as the starting material would make the final product safer for workers at the time of removal. This process seems promising, but it is important to consider its limitations and the ramifications of its short comings.

5.2 Review of EPSCoR Pre-proposal, "Carbon Onion Nanoparticles for Vadose Zone Remediation- the Foam Delivery Approach"

Overall, this pre-proposal looks very promising; however, results from this study will be site-specific since factors such as soil type, porosity, pollutants, depth and pressures must be considered. Summing up the proposal, it focuses on a novel foam-delivery technology designed to distribute carbon-onion nanoparticles to the vadose zone for the sequestration of contaminants. The claim is that foam provides a stable flow to bring nanoparticles to the vadose zone, minimizing waste mobilization and flow bypassing. Carbon-onion nanoparticles will be used due to their cost effectiveness and their ability to sequester and immobilize contaminants due to their massive specific surface area and sorption capacity.

First of all, data on the characteristics of the site to which they are trying to apply this technology should be included as one of the tasks. For instance, information such as soil type and porosity, as it varies with depth, is very important when designing the foam, especially the bubble size ranges, since this will determine the flow characteristics. Also, studies on competitive sorption rates should be included, in which there are realistic environmentally occurring concentrations of different species currently present in the soil, not only heavy metals and radionuclides.

The proposal did not go into detail on the process for selecting the foam-generating surfactant. This is very important since the solution foamability and the influence of foam quality are dependant on the surfactant. Also, because the foam flow is non-Newtonian, finding the most effective surfactant concentration is critical since its mobility and stability are dependent on it. Another factor, which was mentioned as an objective but not developed in the paper, is the extent of heavy-metal and radionuclide immobilization using this approach.

Still, the challenge comes when selecting a surfactant that will not be detrimental to the environment. The toxicity of the surfactant should, therefore, be taken into consideration. Lirong Zhong from PNNL has performed some studies using sodium lauryl ether sulfate (SLES); however, this surfactant actually presents some level of toxicity to humans. Also, when interacting with nitrogen-containing compounds, it may react and form nitrates which are potentially carcinogenic. In addition, on the SLES Material Safety Data Sheet, it is mentioned that "the product is toxic to aquatic organisms," which would be critical in case the substance reaches groundwater. In addition, SLES is an anionic surfactant. Ionic surfactants sorb to the soil material and are removed from the solution. This characteristic of SLES just increases its chances of reaching groundwater since, once sorbed to the soil, gravity may carry the compound to the aquifer. Non-ionic surfactants should be considered for this type of applications since they do not sorb as strongly as ionic surfactants to soil material. In addition, they are less toxic and more biodegradable. On Task II-A, the proposal say they want "to produce highly stable foam." Studies should be made to establish the ideal stability of the foam, since the more stable the foam, the higher the ability for the surfactant to sorb to the soil.

Lirong Zhong has also developed an analytical solution for foam transport where a relationship between foam mobility, quality and injection rate was established. Concurrently, column experiments were carried out to investigate the movement of foam with different quality and injection rates. The results from these studies should be taken into consideration to prevent overlapping of research work.

Carbon nanoparticle's ability to aggregate should be considered in the proposed project. In a study performed by Yang, et al., they found that in a carbon fullerene, the surface available for adsorption is smaller than its calculated surface area. It was also observed that, under laboratory conditions, these nanoparticles may aggregate; it was suggested that the same may occur in the environment. Due to this aggregation, an experimental column set up by E. Ballesteros, et al., filled with carbon fullerene never sorbed more than 60% of the total amount of organic compound that was added to the solution. Therefore, the sorption capacity of the carbon onion nanoparticles under varying conditions should be carefully measured and the possibility of using irregularly shaped nanoparticles, which would prevent the formation of interstitial spaces, should be considered. Another very important issue found by Ballesteros, et al., was that the adsorption efficiency decreased with the increasing polarity of the solute. This is of concern since the surfactant that was considered for use is ionic, which consequently will further decrease the adsorption efficiency of the carbon onion nanoparticles.

Another issue, which might not be part of the scope of the project but should be addressed in the future, is how they will control the foam migration to make sure it reaches the desired regions in the vadose zone.

6. CONCLUSION

The role of the Office of Groundwater and Soil at DOE Headquarters is to incentivize a stronger collaboration with the science and engineering community to find safe, cost-effective, and environmentally sound technical solutions. Their vision and mission lead this initiative as can be seen in this report, specifically in the mercury characterization and remediation action area. Also, project proposal reviews have been performed in collaboration of different DOE programs to stimulate research initiatives, as well as other institutions such as the Department of Defense to make sure any government funded research complies with environmental standards.

7. REFERENCES

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